



Poly(vinylidene fluoride-co-hexafluoropropylene) phase inversion coating as a diffusion layer to enhance the cathode performance in microbial fuel cells

Wulin Yang^a, Fang Zhang^a, Weihua He^b, Jia Liu^a, Michael A. Hickner^c, Bruce E. Logan^{a,*}

^a Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, PA 16802, United States

^b State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, No. 73 Huanghe Road, Nangang District, Harbin 150090, China

^c Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, United States

HIGHLIGHTS

- A PVDF-HFP phase inversion coating produced good resistance to water leakage.
- The PVDF-HFP phase inversion coating enabled higher power production.
- Power production correlated with a more porous diffusion layer.

ARTICLE INFO

Article history:

Received 21 May 2014

Accepted 22 June 2014

Available online 7 July 2014

Keywords:

MFC

Cathode

Water resistant diffusion layer

PVDF-HFP phase inversion coating

Power production

ABSTRACT

A low cost poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) phase inversion coating was developed as a cathode diffusion layer to enhance the performance of microbial fuel cells (MFCs). A maximum power density of $1430 \pm 90 \text{ mW m}^{-2}$ was achieved at a PVDF-HFP loading of 4.4 mg cm^{-2} (4:1 polymer:carbon black), with activated carbon as the oxygen reduction cathode catalyst. This power density was 31% higher than that obtained with a more conventional platinum (Pt) catalyst on carbon cloth (Pt/C) cathode with a poly(tetrafluoroethylene) (PTFE) diffusion layer ($1090 \pm 30 \text{ mW m}^{-2}$). The improved performance was due in part to a larger oxygen mass transfer coefficient of $3 \times 10^{-3} \text{ cm s}^{-1}$ for the PVDF-HFP coated cathode, compared to $1.7 \times 10^{-3} \text{ cm s}^{-1}$ for the carbon cloth/PTFE-based cathode. The diffusion layer was resistant to electrolyte leakage up to water column heights of $41 \pm 0.5 \text{ cm}$ (4.4 mg cm^{-2} loading of 4:1 polymer:carbon black) to $70 \pm 5 \text{ cm}$ (8.8 mg cm^{-2} loading of 4:1 polymer:carbon black). This new type of PVDF-HFP/carbon black diffusion layer could reduce the cost of manufacturing cathodes for MFCs.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Microbial fuel cell (MFC) technologies can be used to convert organic and inorganic substrates to electrical power [1–5]. Exoelectrogenic bacteria on the anode oxidize substrates to generate electrons, which flow through an external circuit to the cathode where typically oxygen reduction occurs. Platinum is often used as the oxygen reduction catalyst in these cathodes [6,7], although different catalysts have also been investigated such as carbon nanotubes, cobalt oxides, and an iron-nitrogen-carbon catalyst [8–10]. Activated carbon (AC) has emerged as the most attractive

alternative catalyst to platinum due to its low cost ($\$2.6 \text{ kg}^{-1}$), and it can have comparable or superior performance to Pt-based catalysts over time in MFCs [11–13].

A typical AC cathode consists of an AC catalyst layer on the electrolyte side that is directly attached to a current collector, and a diffusion layer on the air side. The diffusion layer has two important roles in cathode performance: it serves as a barrier to separate the solution phase from air phase, and therefore to avoid water leakage through the cathode; and it can be used to limit oxygen transfer into the anode solution, but it must allow oxygen to reach the cathode catalyst sites. Hydrophobic polymers, such as polytetrafluoroethylene (PTFE) and poly(dimethylsiloxane) (PDMS), are often used to make diffusion layers [11,14]. Carbon black (CB) is added into these polymers to enhance porosity and thereby improve oxygen mass transfer to the catalyst. A PTFE/CB diffusion

* Corresponding author. Tel.: +1 814 863 7908; fax: +1 814 863 7304.

E-mail address: blogan@psu.edu (B.E. Logan).

layer was previously developed that had good structural rigidity, but forming the cathode required sintering at a high temperature of 340 °C [11]. An alternative diffusion layer made of a PDMS/CB mixture was shown to achieve good oxygen permeability, but no information was provided relative to possible water leakage at higher water pressures that would be encountered when larger cathodes are employed [14]. Improvements in both the oxygen transfer and waterproofing properties of diffusion layers could be useful in improving power production by MFCs, as long as these materials are inexpensive and can easily be formed into the desired cathode profile.

Two polymers that exhibit good physical stability and chemical resistance [15] that could be useful as diffusion layers in MFCs are poly(vinylidene fluoride) (PVDF) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP). These materials are both hydrophobic fluorinated polymers that have long been used for membrane-based processes such as membrane distillation [16,17]. PVDF-HFP may be more useful in MFC applications as the hexafluoropropylene (HFP) group increases the fluorine content, which makes PVDF-HFP more hydrophobic than PVDF [18]. Preparation of porous membranes from these polymers is easily accomplished by the phase inversion process [19]. During phase inversion casting, PVDF-HFP polymer chains precipitate due to non-solvent interactions and form a more flexible structure compared to PVDF as a result of the lower crystallinity of the PVDF-HFP [18]. In order to improve the performance of MFCs, a PVDF-HFP coating was examined as a new type of water resistant diffusion layer that could easily be made using the phase inversion method. The typical preparation of the polymer diffusion layer coating was modified to include inexpensive CB as filler particles to improve the oxygen permeability of the diffusion layer. Different thicknesses and mass ratios of PVDF-HFP and CB in the diffusion layer were examined to improve oxygen transfer and power production, and to minimize water leakage. The effects of different preparation conditions were examined in terms of the mechanical stability of the material relative to oxygen transfer and performance properties.

2. Materials and methods

2.1. Cathode fabrication

The catalyst layer was prepared by mixing AC powder (Norit SX plus, Norit Americas Inc., TX) with a 60% PTFE emulsion and CB at a ratio of 9:1:0.9 (w/w), except as noted. The AC mixture was then spread with a lab spatula onto a 11.3 cm² circular section of stainless steel mesh (corrosion-resistant 304 stainless steel woven wire cloth, 42 × 42 mesh, 0.014 cm wire diameter; McMaster-Carr, USA) and dried in a fume hood for >2 h at room temperature (23 ± 1 °C).

Poly(vinylidene fluoride-co-hexafluoropropylene) (Kynar® Flex 2801, 12 wt.% HFP) was purchased from Arkema, Inc. N, N-Dimethylacetamide (DMAc) was used as the solvent to dissolve the PVDF-HFP. A 10% (w/v) PVDF-HFP solution was stirred vigorously with a magnetic stir bar at room temperature for >8 h to completely dissolve the polymer. The diffusion layer casting solution was then made by combining PVDF-HFP (100 mg, 1 mL of 10% PVDF-HFP solution) with CB at mass ratios of 4:1, 4:2 and 4:3 of PVDF-HFP:CB. After vortexing for 20 s, the solution was spread directly onto the AC catalyst layer with a lab spatula. The cathodes were then immersed into deionized (DI) water for 10 min at room temperature to induce phase inversion. The cathodes were dried in an oven at 80 °C for 5 min, followed by additional air drying in a fume hood for 6 h. The cathodes were stored in DI water prior to testing. Cathodes with different PVDF-HFP loadings (2.6 mg cm⁻², 4.4 mg cm⁻² and 8.8 mg cm⁻²) were also prepared at a ratio of 4:1 of PVDF-HFP:CB.

Scanning electron microscopy (SEM; FEI model XL30, tungsten filament, 5 KeV electron beam) was used to examine the morphology of the PVDF-HFP diffusion layers. The cathodes were dried and then sputter coated with gold particles for SEM imaging. SEM was not done for 2.6 mg cm⁻² loading due to the difficulty to obtain useful images at this low loading.

A carbon cloth-based cathode with platinum catalyst (ETEK C1-10 10% Pt on Vulcan XC-72) and a PTFE diffusion layer was prepared as previously described, and used as a control to evaluate performance relative to the AC [6]. A poly(dimethylsiloxane) (PDMS) wipe diffusion layer was also prepared as previously described [20] to provide a comparison to the diffusion layers tested here. Two layers of PDMS solution were applied to a cloth wipe material (DuPont Sontara, Style 8864), and then this wipe diffusion layer was placed toward the AC catalyst layer.

2.2. Electrochemical measurements

All electrochemical measurements were conducted in an electrochemical cell (2 cm length, 3 cm diameter) containing two chambers separated by a Nafion® membrane. The electrolyte was a 50 mM phosphate buffer solution (PBS) (Na₂HPO₄, 4.58 g L⁻¹; NaH₂PO₄·H₂O, 2.45 g L⁻¹; NH₄Cl, 0.31 g L⁻¹; KCl, 0.31 g L⁻¹; pH = 6.9; κ = 6.94 mS cm⁻¹). The counter electrode was a 7 cm² round platinum plate. An Ag/AgCl reference electrode (RE-5B, BASi, West Lafayette, IN; +0.209 V versus a standard hydrogen electrode) was placed close to cathode and kept in the same position for each test. All potentials were reported here versus SHE. A potentiostat (VMP3 Multichannel Workstation, Biologic Science Instruments, USA) was used for all measurements in a constant temperature room (30 °C).

A step current method was used to obtain the cathode polarization curve by applying different currents after keeping the cell in an open circuit condition for 1 h. The lower currents (1 mA, 2 mA, 3 mA and 4 mA) were applied for 1 h and the higher currents (5 mA, 6 mA, 7 mA, 8 mA, 9 mA and 10 mA) were applied for 30 min to obtain steady-state conditions.

2.3. MFC Construction and operation

MFCs were single-chamber, cubic reactors 4 cm in length with an inside diameter of 3 cm. The anodes were graphite fiber brushes heat treated at 450 °C in air for 30 min [21]. The MFC anodes were fully acclimated through operation for over one year at a fixed external resistance of 1000 Ω in a constant temperature room (30 °C). The medium contained 1 g L⁻¹ sodium acetate dissolved in 50 mM PBS buffer with trace minerals and vitamins [22].

Single cycle polarization tests were conducted by varying the external resistance from 1000 to 20 Ω at 20 min intervals. Voltage drops (U) across external resistors were recorded by a computer based data acquisition system (2700, Keithley Instrument, OH). Current densities (i) and power densities (P) were normalized to the projected working cathode area ($A = 7$ cm²), and calculated as $i = U/RA$ and $P = iU/A$, where R is the external resistance. To avoid power overshoot in PVDF-HFP diffusion layer loading tests, multiple cycle polarization tests were conducted by using a different external resistance (1000–20 Ω) over a complete fed-batch cycle (as indicated). All polarization data were obtained after 5 fed-batch cycles to ensure steady state. Current densities and power densities were based on the maximum power during each cycle. Cathode impedance was calculated from the slope of cathode polarization curve, and normalized by the projected working cathode area. Coulombic efficiencies were calculated for each resistance as previously described based on changes in chemical oxygen demand (COD) concentration [23]. All tests were conducted in duplicate.

2.4. Oxygen permeability

Oxygen transport through the cathode was calculated in terms of an oxygen mass transfer coefficient (k , cm s^{-1}) based on the change in the dissolved oxygen (DO) concentration in a 4 cm long single-chamber reactor as previously described (duplicate measurements) [6]. Dissolved oxygen (DO) concentrations were measured using a non-consumptive DO probe (Foxy-18G, Ocean Optics Inc., USA).

2.5. Pressure tests

A fully assembled reactor was used to determine the maximum water pressure (in cm of static head) that would produce water leakage through the cathodes (Fig. S1). A cubic single-chamber MFC was connected through a hole on its side using a rubber tube to a water storage bottle. The height of water was changed by raising the storage container until water droplets were observed on the air side of the cathode diffusion layer. The static pressure head (cm) was calculated as the difference in height between the cathode and the top of the water level in the storage container.

3. Results and discussion

3.1. MFC performance with different polymer ratios

MFC tests were first conducted with cathodes composed of different polymer to carbon black ratios. A maximum power density of $1390 \pm 175 \text{ mW m}^{-2}$ was achieved with the 4:1 PVDF-HFP:CB diffusion layer, which contained 8.8 mg cm^{-2} of PVDF-HFP and 2.2 mg cm^{-2} of CB. A similar maximum power density of $1430 \pm 150 \text{ mW m}^{-2}$ was achieved with the 4:2 PVDF-HFP:CB diffusion layer, which contained 8.8 mg cm^{-2} of PVDF-HFP and 4.4 mg cm^{-2} of CB. The lowest power density of $1280 \pm 330 \text{ mW m}^{-2}$ was produced using the 4:3 polymer:CB diffusion layer (Fig. 1A). Increasing the ratio of polymer to CB led to a less mechanically stable diffusion layer, as cracks were observed for layers with 4:3 PVDF-HFP:CB. Generally, no large differences in power performance were observed with different diffusion layer polymer:CB composition ratios, based on similar cathode potentials (Fig. 1B).

3.2. Electrochemical performance of cathodes as a function of polymer loading

Further tests were conducted to examine the effect of polymer loading, all at the 4:1 ratio for PVDF-HFP:CB. Cathode polarization tests conducted using an abiotic electrochemical cell showed that the AC cathode with a diffusion layer polymer loading of 4.4 mg cm^{-2} PVDF-HFP had the best electrochemical performance (Fig. 2). The AC cathode with a diffusion layer of the same polymer loading and phase inversion processing, but without CB, had the poorest electrochemical performance. The use of CB as filler particles in the PVDF-HFP polymer therefore greatly improved cathode performance, likely by introducing porosity into the polymer layer. The cathode with a polymer loading of 8.8 mg cm^{-2} (4:1 polymer:CB) showed slightly better performance than the one with the lowest loading (2.6 mg cm^{-2} , 4:1 polymer:CB).

The Pt/C-based cathode had better electrochemical performance than the AC-based cathode with a 2.6 mg cm^{-2} loading at both high and low current densities, but it performed worse at intermediate current densities ($4\text{--}6 \text{ A m}^{-2}$), perhaps due to dihydrogen phosphate adsorption on catalytic sites [24].

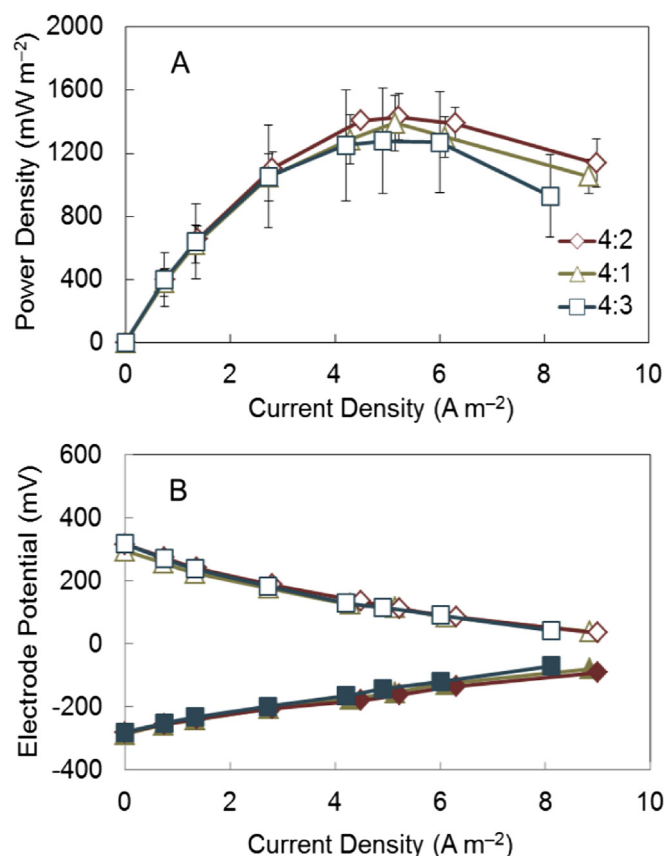


Fig. 1. (A) Power density curve for ratio test (4:1, 4:2 and 4:3 corresponding to PVDF-HFP:CB in mass ratio) (B) Electrode potentials (solid symbols for anode potentials and open symbols for cathode potentials).

3.3. MFC Performance as a function of polymer loading

When the cathodes with different PVDF-HFP loading were used in MFCs, the best performance was obtained using the diffusion layer with 4.4 mg cm^{-2} loading (4:1 ratio of PVDF-HFP:CB), in agreement with abiotic electrochemical tests (Fig. 3A). The largest maximum power density for this cathode was $1430 \pm 90 \text{ mW m}^{-2}$. Increasing or decreasing this PVDF-HFP loading reduced performance. The maximum power densities were $1280 \pm 60 \text{ mW m}^{-2}$

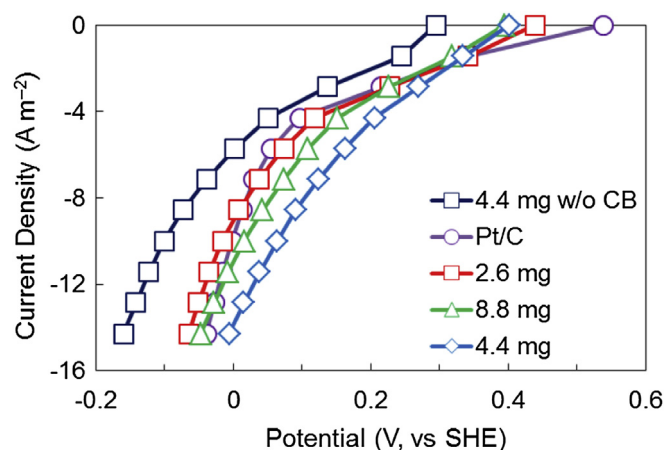


Fig. 2. Current-voltage (polarization) curves using AC cathodes with different loading of PVDF-HFP and Pt/C cathode.

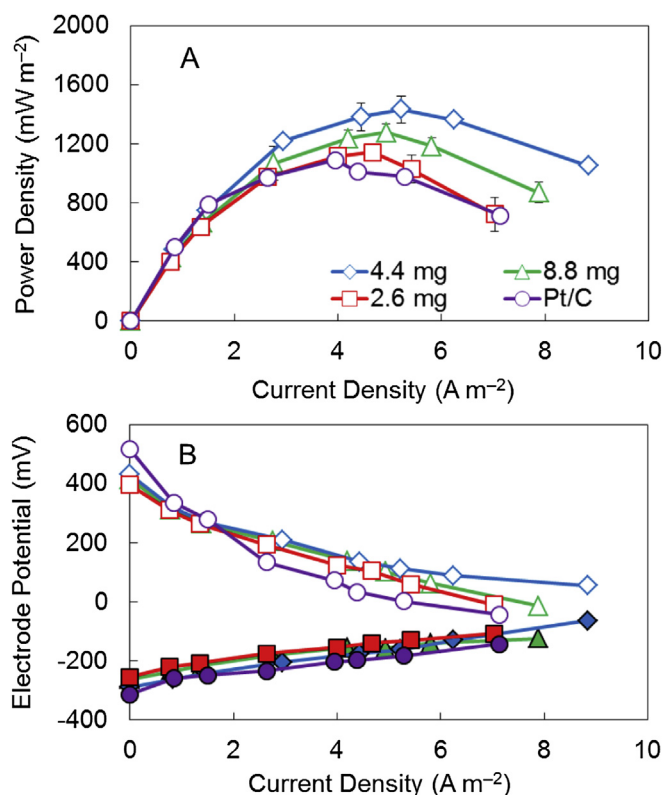


Fig. 3. (A) Power density curve for PVDF-HFP loading test (normalized to cm²) at 4:1 ratio and Pt/C cathode (B) Electrode potentials (solid symbols for anode potentials and open symbols for cathode potentials).

with a higher loading (8.8 mg cm⁻²), and 1140 ± 60 mW m⁻² at the lower loading (2.6 mg cm⁻²). All of these power densities were slightly higher than those produced with the Pt/C cathode of 1090 ± 30 mW m⁻². The cathodic polarization curves also showed that Pt/C cathode had a lower cathode potential than the other three AC cathodes (Fig. 3B), indicating the anode performance was not a factor.

The cathode resistances followed a trend consistent with whole cell polarization data, with the resistances varying inversely with maximum power densities. The Pt/C-based cathode had the largest resistance of 110 ± 6 Ω, followed by the AC cathodes with different PVDF-HFP loadings that had resistances of 75 ± 6 Ω (2.6 mg cm⁻²), 69 ± 7 Ω (8.8 mg cm⁻²), and 61 ± 2 Ω (4.4 mg cm⁻²).

MFCs with the cathode PVDF-HFP diffusion layer developed here produced a higher power density, and used less polymer, than MFCs with diffusion layers made of other polymers such as PDMS and PTFE. A diffusion layer consisting of PDMS and CB applied to a wipe cloth, with a similar cathode structure and the same type of MFC, produced a maximum power density of 1310 ± 70 mW m⁻² [20]. A PTFE/CB diffusion layer rolled onto stainless steel mesh produced a maximum of power density 1360 ± 30 mW m⁻² [25]. Both of these power densities are lower than the maximum power densities obtained here. The optimum PVDF-HFP diffusion layer required less polymer and CB (4.4 mg cm⁻² of polymer and 1.1 mg cm⁻² of CB), compared to the PDMS wipe (12.1 mg cm⁻² of PDMS and 3.1 mg cm⁻² of CB) [14] or the PTFE (45 mg cm⁻² of polymer and 19.1 mg cm⁻² of CB) (Personal communication, Xin Wang) diffusion layers. The PVDF polymer was also less expensive, so that polymer costs for these this diffusion layers was only \$1.1 m⁻² for PVDF-HFP (\$25 kg⁻¹), compared to \$0.36 m⁻² for PDMS (\$3 kg⁻¹) and \$11 m⁻² for PTFE (\$25 kg⁻¹) diffusion layers [26]. In addition, the PTFE/CB diffusion layer requires sintering at

340 °C for 25 min, which makes its preparation more complicated and expensive [25] than the other types of diffusion layers.

3.4. Coulombic efficiencies

MFCs with Pt/C-based cathodes showed the highest CEs at all current densities and reached a maximum CE of 79% at a current

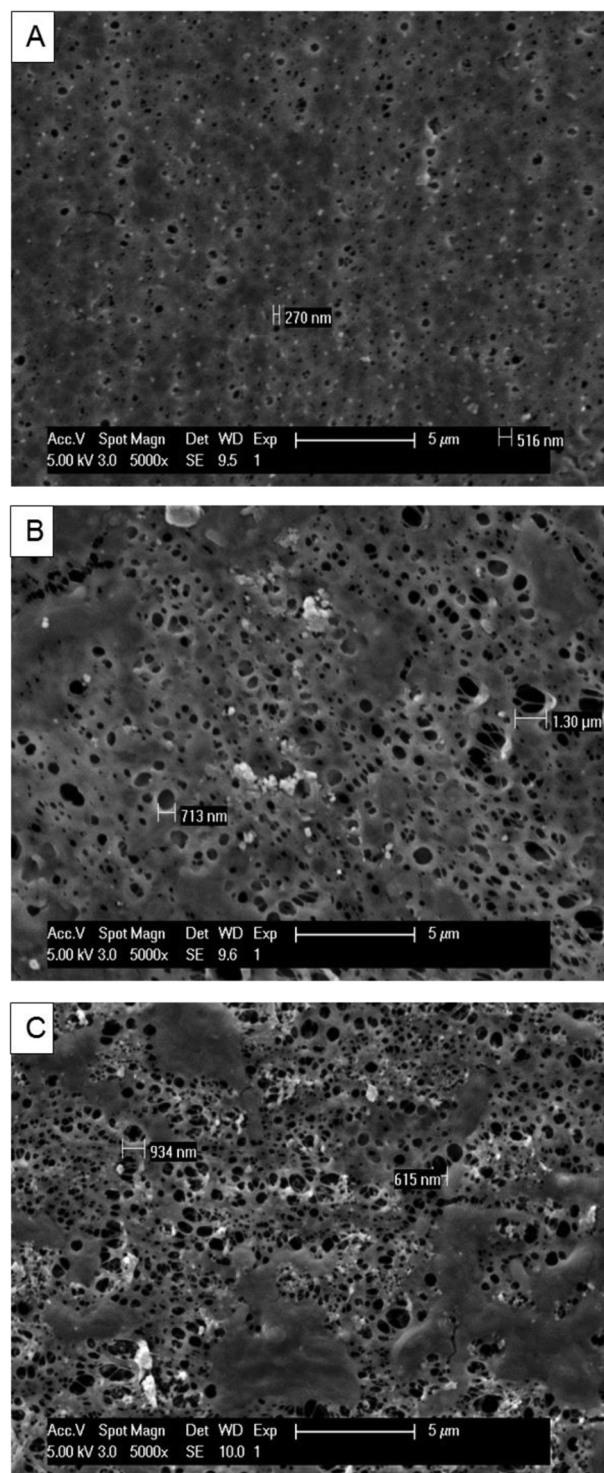


Fig. 4. SEM images of PVDF-HFP diffusion layer with (A) 4.4 mg cm⁻² loading without CB (B) 8.8 mg cm⁻² loading with CB at the ratio of 4:1 PVDF-HFP:CB (C) 4.4 mg cm⁻² loading with CB at the ratio of 4:1 PVDF-HFP:CB.

density of 7.1 A m^{-2} (Fig. 5A). This CE was much larger than the highest CE of 60% produced using the 4.4 mg cm^{-2} PVDF-HFP loading (4:1 polymer:CB). The CEs all increased with the current density, which is commonly observed for MFCs using acetate [27].

3.5. Surface morphology

Based on the SEM images, the addition of the CB resulted in a more porous PVDF-HFP diffusion layer, and the CB particles were well-distributed within the PVDF-HFP network. A diffusion layer made with the pure polymer showed small surface pore sizes of $<500 \text{ nm}$ (Fig. 4A). When CB was added, larger surface pores were observed at both PVDF-HFP loadings of 8.8 mg cm^{-2} (4:1 polymer:CB) and 4.4 mg cm^{-2} (4:1 polymer:CB) (Fig. 4B and C). The number of pores appeared to have increased with CB addition.

3.6. Oxygen permeability

The oxygen mass transfer coefficient of AC cathodes was inversely related to the loading of PVDF-HFP. With the highest PVDF-HFP loading of 8.8 mg cm^{-2} , at a ratio of 4:1 PVDF-HFP:CB, the oxygen permeability was $1.4 \pm 0.7 \times 10^{-3} \text{ cm s}^{-1}$, which was comparable to the standard Pt/C carbon cloth/PTFE-based cathode with a value of $1.7 \pm 0.8 \times 10^{-3} \text{ cm s}^{-1}$. AC cathodes with an intermediate PVDF-HFP loading of 4.4 mg cm^{-2} and a polymer:CB ratio of 4:1 had an oxygen mass transfer coefficient of $3.1 \pm 0.7 \times 10^{-3} \text{ cm s}^{-1}$, which was the second largest among the cathodes. The mass transfer coefficient increased to $5.4 \pm 1.2 \times 10^{-3} \text{ cm s}^{-1}$ using the lowest PVDF-HFP loading (Fig. 5B).

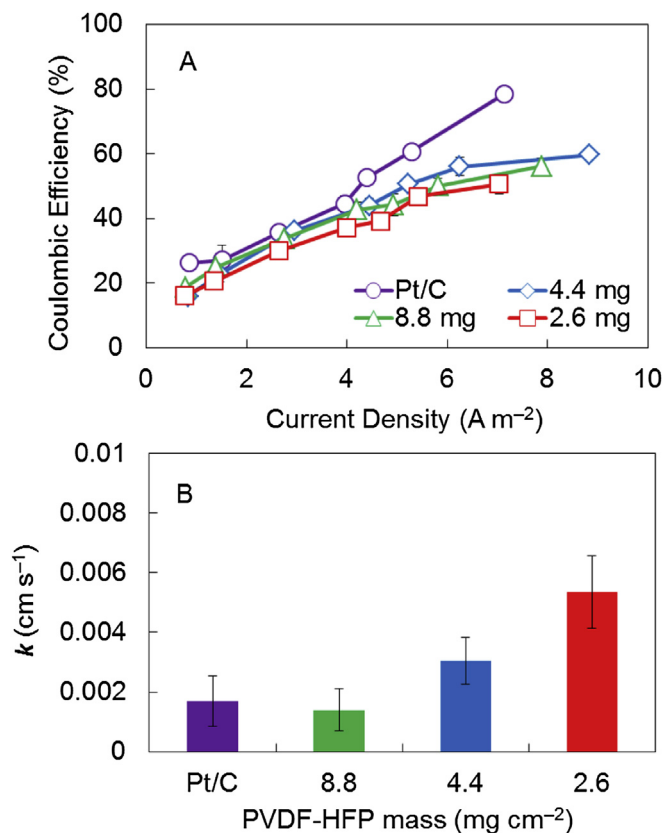


Fig. 5. (A) Coulombic efficiencies (CEs) obtained for PVDF-HFP loading test at 4:1 ratio and Pt/C cathode (B) Oxygen mass transfer coefficient of AC cathodes with different PVDF-HFP loadings and Pt/C cathode.

High oxygen mass transfer should be beneficial for the oxygen reduction reaction, but oxygen transfer alone did not account for the differences in the maximum power densities. AC cathodes with the highest power of $1430 \pm 90 \text{ mW m}^{-2}$ had an intermediate oxygen mass transfer coefficient ($3.1 \pm 0.7 \times 10^{-3} \text{ cm s}^{-1}$) (Fig. 5B). Although the cathode with a 2.6 mg cm^{-2} PVDF-HFP loading with a polymer:CB ratio of 4:1 showed the highest oxygen permeability of the cathodes tested, this diffusion layer resulted in low power ($1140 \pm 60 \text{ mW m}^{-2}$), perhaps as a result of water intrusion (flooding) of the catalyst [28].

3.7. Water pressure tests

The microporous structure of PVDF-HFP diffusion layers (Fig. 4B and C) prevented liquid water leakage through the pores where oxygen enters the cathode structure. Water leakage was only detected on the diffusion layer edges where the cathode was clamped using a gasket to the cell, suggesting the primary reason for leakage was low tensile strength and cracking at the seal edges. Higher loadings of PVDF-HFP greatly increased the water pressure that the cathode could sustain without leaking around the edges. For the PVDF-HFP diffusion layer with 8.8 mg cm^{-2} loading and a polymer:CB ratio of 4:1, the AC-based cathode withstood $70 \pm 5 \text{ cm}$ of water pressure (Fig. 6). With lower loadings of 4.4 and 2.6 mg cm^{-2} at the same polymer:CB ratio, the water pressures that AC cathode was able to withstand before leakage decreased to $41 \pm 0.5 \text{ cm}$ and $2 \pm 0.5 \text{ cm}$, respectively, suggesting further decreases of the PVDF-HFP loading might compromise the physical and mechanical strength of this coating. The PDMS/CB wipe-based diffusion layer withstood a water pressure of only $19 \pm 1 \text{ cm}$, while the Pt/C-based standard cathode started leaking through the pores at $120 \pm 7 \text{ cm}$ (Fig. 6).

4. Conclusions

A microporous diffusion layer with a PVDF-HFP loading of 4.4 mg cm^{-2} and CB loading of 1.1 mg cm^{-2} (mass ratio of 4:1 of PVDF-HFP:CB) had good electrochemical performance and required less polymer than previously prepared cathodes. The maximum power was $1430 \pm 90 \text{ mW m}^{-2}$ with 4.4 mg cm^{-2} PVDF-HFP loading (4:1 loading ratio), compared to $1090 \pm 30 \text{ mW m}^{-2}$ for the Pt/C cathode with a PTFE diffusion layer. The PVDF-HFP diffusion layer withstood a water pressure of $41 \pm 0.5 \text{ cm}$ water height with a polymer loading of 4:1 (polymer:CB), with leakage around the cathode edges but not through the pores. These results

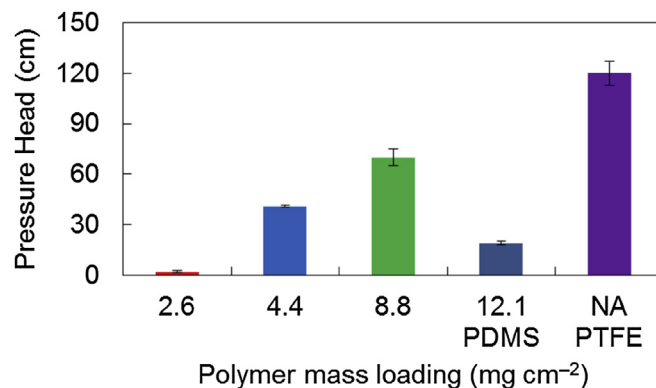


Fig. 6. Water pressure resistance of cathodes with different diffusion layer polymer loadings.

suggest that PVDF-HFP phase inversion diffusion layer could be useful as a lower cost way to construct MFC cathodes.

Acknowledgments

This research was supported by the Strategic Environmental Research and Development Program (SERDP) Project ER-2216, Award KUS-I1-003-13 from the King Abdullah University of Science and Technology (KAUST), and a graduate scholarship from the China Scholarship Council (CSC) to W. Y.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.06.119>.

References

- [1] B.E. Logan, *Microbial Fuel Cells*, John Wiley & Sons, Inc., Hoboken, NJ, 2008.
- [2] J. Niessen, U. Schröder, F. Scholz, *Electrochem. Commun.* 6 (2004) 955–958.
- [3] R.M. Allen, H.P. Bennetto, *Appl. Biochem. Biotechnol.* 39 (1993) 27–40.
- [4] D.R. Bond, D.E. Holmes, L.M. Tender, D.R. Lovley, *Science* 295 (2002) 483–485.
- [5] D.R. Lovley, *Nat. Rev. Microbiol.* 4 (2006) 497–508.
- [6] S. Cheng, H. Liu, B.E. Logan, *Electrochem. Commun.* 8 (2006) 489–494.
- [7] C. Santoro, B. Li, P. Cristiani, G. Squadrito, *Int. J. Hydrogen Energy* 38 (2013) 692–700.
- [8] M. Ghasemi, M. Ismail, S.K. Kamarudin, K. Saeedfar, W.R.W. Daud, S.H.A. Hassan, L.Y. Heng, J. Alam, S.-E. Oh, *Appl. Energy* 102 (2013) 1050–1056.
- [9] J. Ahmed, Y. Yuan, L. Zhou, S. Kim, J. Power Sources 208 (2012) 170–175.
- [10] F. Jaouen, V. Goellner, M. Lefevre, J. Herranz, E. Proietti, J.P. Dodelet, *Electrochim. Acta* 87 (2013) 619–628.
- [11] H. Dong, H. Yu, X. Wang, Q. Zhou, J. Feng, *Water Res.* 46 (2012) 5777–5787.
- [12] S. Cheng, J. Wu, *Bioelectrochemistry* 92 (2013) 22–26.
- [13] F. Zhang, S. Cheng, D. Pant, G.V. Bogaert, B.E. Logan, *Electrochem. Commun.* 11 (2009) 2177–2179.
- [14] F. Zhang, T. Saito, S. Cheng, M.A. Hickner, B.E. Logan, *Environ. Sci. Technol.* 44 (2010) 1490–1495.
- [15] F. Liu, N.A. Hashim, Y.T. Liu, M.R.M. Abed, K. Li, J. Membr. Sci. 375 (2011) 1–27.
- [16] M.C. Garcia-Payo, M. Essalhi, M. Khayet, J. Membr. Sci. 347 (2010) 209–219.
- [17] K.Y. Wang, T.S. Chung, M. Gryta, *Chem. Eng. Sci.* 63 (2008) 2587–2594.
- [18] L. Shi, R. Wang, Y.M. Cao, C.S. Feng, D.T. Liang, J.H. Tay, *J. Membr. Sci.* 305 (2007) 215–225.
- [19] M. Tomaszewska, *Desalination* 104 (1996) 1–11.
- [20] B. Wei, J.C. Tokash, G. Chen, M.A. Hickner, B.E. Logan, *RSC Adv.* 2 (2012) 12751–12758.
- [21] B.E. Logan, S. Cheng, V. Watson, G. Estadt, *Environ. Sci. Technol.* 41 (2007) 3341–3346.
- [22] D.R. Lovley, E.J.P. Phillips, *Appl. Environ. Microbiol.* 54 (1988) 1472–1480.
- [23] B.E. Logan, P. Aelterman, B. Hamelers, R. Rozendal, U. Schröder, J. Keller, S. Freguiau, W. Verstraete, K. Rabaey, *Environ. Sci. Technol.* 40 (2006) 5181–5192.
- [24] I.S.P. Savizi, M.J. Janik, *Electrochim. Acta* 56 (2011) 3996–4006.
- [25] H. Dong, H. Yu, X. Wang, *Environ. Sci. Technol.* 46 (2012) 13009–13015.
- [26] www.alibaba.com.cn, Plastic Source Market.
- [27] Y. Fan, H. Hu, H. Liu, J. Power Sources 171 (2007) 348–354.
- [28] F. Zhang, G. Chen, M.A. Hickner, B.E. Logan, *J. Power Sources* 218 (2012) 100–105.